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IN THE UNITED STATE PATENT AND TRADEMARK OFFICE

In re Patent application of :
Sang-Jun Choi : Group Art Unit: 1752
Serial No. 09/715,041 : Examiner Yvette C. Thornton
Filed November 20, 2000 :

**PHOTORESISTIVE POLYMER HAVING CYCLIC BACKBONE AND RESIST
COMPOSITION CONTAINING THE SAME**

VERIFYING DECLARATION

Honorable Commissioner For Patents
Washington, D.C. 20231

Sir:

I, Soonae Kim, declare and say:
(print name of translator)

that I am thoroughly conversant in both the Korean and English languages;

that I am presently engaged as a translator in these languages; and

that the attached is a true and accurate English language translation of
the "Invention Disclosure" attached to the DECLARATION OF SANG-JUN CHOI
UNDER 37 C.F.R. 1.131.

Signed this 7th day of Jan., 2005.

Soonae Kim
(signature of translator)

INVENTION DISCLOSURE

Title of Invention

5 Photosensitive Polymer and Resist Composition Containing the Same

Background Art & Objects of the Invention

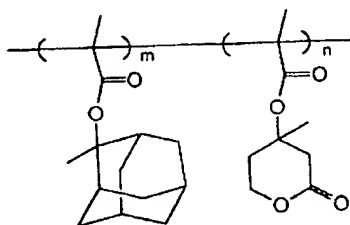
10 As semiconductor devices become highly integrated, fine pattern formation is required in a photolithography process. Further, as the capacity of a semiconductor device increases to exceed 1 giga bit DRAM grade, a pattern size having a design rule of less than 0.2 μm is required. Accordingly, there are limitations in using a conventional resist material with a KrF excimer laser (248 nm). Thus, new resist materials capable of being developed using an ArF excimer laser (193 nm) have
15 been developed for a lithography process. The resist materials used in the lithography process using the ArF excimer laser have several problems in being commercially used, compared to the conventional resist materials.

20 The most typical problems are transmittance of a polymer and resistance to dry etching. As the widely known ArF resist materials, (meth)acrylate polymers are generally used. In particular, the most typical resist material is poly(methyl methacrylate-tert-butyl methacrylate-methacrylic acid) terpolymer system manufactured by IBM, Inc. However, such polymers have very weak resistance to dry etching. Accordingly, to increase the resistance to dry etching, a polymer having a backbone composed of an alicyclic compound such as an isobornyl group, an
25 adamantyl group or a tricyclodecanyl group, is used. However, the resulting resist still exhibits weak resistance to dry etching. The polymer having the alicyclic compound is less adhesive to a layer, thereby causing lifting effects of a resist pattern during a developing process.

30 Recently, as new types of polymers, a methacrylate copolymer compound having an alicyclic protecting group (formula 1) manufactured by Fujitsu and a cycloolefine-maleic anhydride (COMA) alternating polymer (formula 2) manufactured by IBM, Inc. have been proposed (see *J. Photopolym. Sci. Technol.*, 12(3), 501 (1999)). However, the polymers have problems and are not suitable to be used as ArF resists. The polymer having formula 1 has problems, such as weak resistance

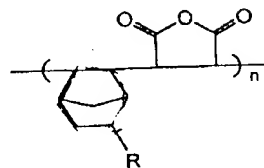
to dry etching and deteriorated line edge roughness (LER) and the polymer having formula 2 has deteriorated resist contrast and low transmittance.

Formula 1



- High contrast
- Line edge roughness
- Poor etch resistance
- High cost

Formula 2



- Good etch resistance
- Low transmittance
- Low synthetic yield
- Poor adhesion

Accordingly, to overcome the above problems of the conventional polymers and obtain a resist having a high lithographic performance, the present inventors conducted research and produced a new type of polymer, which is a copolymer of maleic anhydride monomer and meth(acrylate) monomer having a bulky alicyclic protecting group. The polymer has remarkably higher transmittance and synthetic yield than the conventional COMA system. In addition, the polymer can have superior resistance to etching and has an advantage in view of production costs, compared to methacrylate copolymer in the prior art.

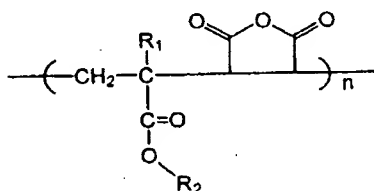
In general, since a maleic anhydride monomer cannot be polymerized in itself, the monomer is used in a polymerization process in a form of an alternating copolymer with olefin monomer substituted with an electron-donating group and alkyl vinyl ether and cycloolefin, etc. are most frequently used as comonomers. Meanwhile, in the present invention, the copolymer with meth(acrylate) monomer substituted with the electron-donating group can be produced in a form of homopolymer or copolymer according to polymerization conditions and constitutional ratios of the monomers. If necessary, a terpolymer or higher copolymer may be produced by introducing a second or a third monomer to a reaction mixture to control polarity of the polymer.

Also, the polymer according to the present invention has a polymer backbone such that a problem of post-exposure delay (PED) due to high T_g (glass transition

temperature) ($> 180^{\circ}\text{C}$) resulting from a rigid backbone which is a drawback of the conventional COMA alternating copolymer can be overcome. Thus, the present polymer has T_g within a suitable range ($130\text{-}160^{\circ}\text{C}$) and can improve PED due to an annealing effect in proceeding processes. Moreover, by introducing an acrylate monomer in place of an cycloolefin monomer, more appropriate polymer polarity can be obtained and thus, adhesion to underlying layers can be improved.

More specifically, the present invention provides a substance having the following formula 3:

Formula 3



wherein

R_1 is hydrogen or methyl group,

R_2 is a group which can be decomposed by an acid generated due to exposure to light, especially an alicyclic tert-alkyl group.

That is, R_2 is a bulky tertiary alkyl group containing an alicyclic ring structure, such as 2-methyl-2-norbornyl, 2-ethyl-2-norbornyl, 2-methyl-2-isobornyl, 2-ethyl-2-isobornyl, 8-methyl-8-tricyclo[5.2.1.0^{2,6}]decanyl, 8-ethyl-8-tricyclo[5.2.1.0^{2,6}]decanyl, 2-methyl-2-adamantyl, or 2-ethyl-2-adamantyl, and increases resistance to etching and functions as a dissolution inhibitor. When a maleic anhydride monomer is introduced, it functions as an adhesion promoter and increases wettability, etc.

As a result, the copolymer according to the present invention can overcome the problems of the conventional polymers and can be produced in a simpler manner and with lower costs. When a resist composition containing the polymer according to the present invention is used in various photolithographic processes, the resist composition can have excellent lithographic performance and be very useful in manufacturing a next generation of semiconductor devices.

Detailed Disclosure of the Invention

Example 1

Synthesis of 8-ethyl-8-tricyclodecanol

200 ml of a solution of ethyl magnesium bromide (1.0 M) in diethyl ether was put into a 500 ml three-neck rounded-bottom flask and tricyclodecan-8-one (30 g, 0.2 mol) dissolved in diethyl ether was slowly dropped in the flask at room temperature using a dropping funnel, and was then reacted in a reflux condition for about 12 hours.

After the reaction was completed, the resultant product was poured into an excess amount of water and neutralized using HCl. Thereafter, the resultant produce was extracted using diethyl ether and dried using MgSO_4 . Then, the solvent was evaporated and a desired product was separated from the crude product using column chromatography (yield: 65 %).

Example 2

Synthesis of 8-ethyl-8-tricyclodecanyl acrylate

18 g (0.1 mol) of 8-ethyl-8-tricyclodecanol synthesized in Example 1 and 11 g (0.11 mol) of triethylamine were dissolved in 200 ml of anhydrous tetrahydrofuran (THF) and 10 g (0.11 mol) of acryloyl chloride was slowly added thereto at room temperature, and then the reactants were reacted for about 12 hours.

After the reaction was completed, an excess amount of solvent was evaporated, and the resultant product was poured into an excess amount of water and neutralized using HCl. Thereafter, the resultant product was extracted using diethyl ether and dried using MgSO_4 . Then, the solvent was evaporated and a desired product was separated from the crude product using column chromatography (yield: 75 %).

Example 3

Synthesis of 8-ethyl-8-tricyclodecanyl methacrylate

18 g (0.1 mol) of 8-ethyl-8-tricyclodecanol synthesized in Example 1 and 11 g (0.11 mol) of triethylamine were dissolved in 200 ml of anhydrous THF and 0.11 mol of methacryloyl chloride was added and reacted in the same manner as in Example

2. Then, a desired product was separated in the same manner as in Example 2 (yield: 75 %).

Example 4

Synthesis of 8-methyl-8-tricyclodecanyl acrylate

8-ethyl-8-tricyclodecanol was synthesized in the same manner as in Example 1 using a methyl magnesium bromide solution, and then a desired product was separated using 8-ethyl-8-tricyclodecanol in the same manner as in Example 2.

Example 5

Synthesis of 2-methyl-2-adamantyl acrylate

17 g (0.1 mol) of 2-methyl-2-adamantanol and 11 g (0.11 mol) of triethylamine were dissolved in 250 ml of anhydrous THF and 10 g (0.11 mol) of acryloyl chloride was slowly added thereto at room temperature, and then the reactants were reacted for about 12 hours.

After the reaction was completed, an excess amount of solvent was evaporated, and the resultant product was poured into an excess amount of water and neutralized using HCl. Thereafter, the resultant product was extracted using diethyl ether and dried using MgSO_4 . Then, the solvent was evaporated and a desired product was separated from the crude product using vacuum distillation (yield: 75 %).

Example 6

Synthesis of 2-methyl-2-adamantyl methacrylate

A desired product was obtained in the same manner as Example 5 using 17 g (0.1 mol) of 2-methyl-2-adamantanol, 11 g (0.11 mol) of triethylamine, and 0.11 mol of methacryloyl chloride in 250 ml of anhydrous THF (yield: 75 %).

Example 7

Synthesis of 2-methyl-2-isobornyl acrylate

A solution of camphor (0.2 mol) dissolved in diethyl ether was slowly dropped into 200 ml of a 1.0 M solution of methyllithium dissolved in diethyl ether at room temperature using a dropping funnel and reacted for about 2 hours, and then 20 g

(0.22 mol) of acryloyl chloride was slowly added thereto at room temperature. Then, the reactants were reacted in a reflux condition for about 12 hours.

After the reaction was completed, the resultant product was poured into an excess amount of water and neutralized using HCl. Thereafter, the resultant product was extracted using diethyl ether and dried using MgSO₄. Then, the solvent was evaporated and a desired product was separated from the crude product using vacuum distillation (yield: 65 %).

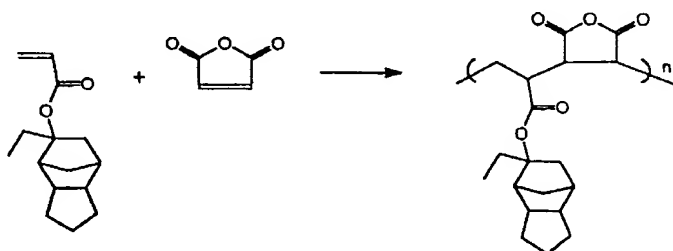
Example 8

Synthesis of 2-methyl-2-norbornyl acrylate

A desired product was obtained in the same manner as Example 7 using 200 ml of a 1.0 M solution of methyllithium dissolved in diethyl ether, a solution of 0.2 mol of norcamphor dissolved in diethyl ether, and 20 g (0.22 mol) of acryloyl chloride (yield: 65 %).

Example 9

Synthesis of copolymer



7.03 g (30 mmol) of 8-ethyl-8-tricyclodecanyl acrylate synthesized in Example 2, 2.94 g (30 mmol) of maleic anhydride and azobis(isobutyronitrile) (AIBN) (1 mol%) were dissolved in 40 g of anhydrous THF, and purged using nitrogen gas for about 1 hour. Thereafter, the reactants were polymerized at 70°C for about 12 hours.

After the polymerization was completed, the resultant product was slowly dropped into an excess amount of n-hexane and precipitated. The obtained precipitate was dissolved in THF and reprecipitated twice in a co-solvent system

(n-hexane : isopropyl alcohol=1:1). Then, the precipitate was dried in a vacuum oven maintained at 50°C for about 24 hours to obtain a desired polymer (yield: 70%).

The weight-average molecular weight (Mw) and polydispersity of the obtained product were 11,800 and 2.1, respectively.

5

Example 10

Synthesis of copolymer

30 mmol of 8-ethyl-8-tricyclodecanyl methacrylate synthesized in Example 3, 30 mmol of maleic anhydride and AIBN (1 mol%) were dissolved in 40 g of anhydrous THF and polymerization was carried out in the same manner as in Example 9.

10

After polymerization was completed, a desired polymer was obtained in the same manner as in Example 9 (yield: 65%).

The weight-average molecular weight (Mw) and polydispersity of the obtained product were 12,300 and 2.1, respectively.

15

Example 11

Synthesis of copolymer

30 mmol of 8-methyl-8-tricyclodecanyl acrylate synthesized in Example 4, 30 mmol of maleic anhydride and AIBN (1 mol%) were dissolved in 40 g of anhydrous THF and polymerization was carried out in the same manner as in Example 9.

20

After polymerization was completed, a desired polymer was obtained in the same manner as in Example 9 (yield: 70%).

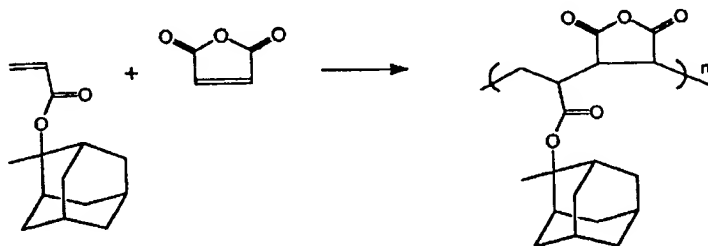
The weight-average molecular weight (Mw) and polydispersity of the obtained product were 12,300 and 2.1, respectively.

25

Example 12

Synthesis of copolymer

30



6.61 g (30 mmol) of 2-methyl-2-adamantyl acrylate synthesized in Example 5, 2.94 g (30 mmol) of maleic anhydride and AIBN (1 mol%) were dissolved in 40 g of anhydrous THF, and purged using nitrogen gas for about 1 hour. Thereafter, the reactant was polymerized at 70°C for about 12 hours.

After the polymerization was completed, the resultant product was slowly dropped into an excess amount of n-hexane and precipitated, dissolved again in THF and reprecipitated twice in a co-solvent system (n-hexane : isopropyl alcohol=1:1). Then, the precipitate was dried in a vacuum oven maintained at 50°C for about 24 hours to obtain a desired polymer (yield: 70%).

The weight-average molecular weight (Mw) and polydispersity of the obtained product were 11,100 and 2.0, respectively.

Example 13

Synthesis of copolymer

30 mmol of 2-methyl-2-isobornyl acrylate synthesized in Example 7, 30 mmol of maleic anhydride and AIBN (1 mol%) were dissolved in 40 g of anhydrous THF and then polymerization was carried out in the same manner as in Example 12, to obtain a polymer (yield: 70%).

The weight-average molecular weight (Mw) and polydispersity of the obtained product were 10,800 and 2.2, respectively.

Example 14

Synthesis of copolymer

30 mmol of 2-methyl-2-norbornyl acrylate synthesized in Example 8, 30 mmol of maleic anhydride and AIBN (1 mol%) were dissolved in 40 g of anhydrous THF and polymerization was carried out in the same manner as in Example 12, to obtain a polymer (yield: 70%).

The weight-average molecular weight (Mw) and polydispersity of the obtained product were 12,100 and 2.1, respectively.

Example 15

Synthesis of terpolymer

35 mmol of 8-ethyl-8-tricyclodecanyl methacrylate synthesized in Example 3, 40 mmol of maleic anhydride, 5 mmol of methacrylic acid and AIBN (1 mol%) were

dissolved in 40 g of anhydrous THF, and polymerization was carried out in the same manner as in Example 12, to obtain a polymer (yield: 70%).

The weight-average molecular weight (Mw) and polydispersity of the obtained product were 12,400 and 2.1, respectively.

Example 16

Resist composition for patterning process

- Resist coating: Each of the polymers synthesized in Examples 9 through 15 (12 to 15% by weight of solid matter based on the total weight of a solvent to be obtained) and various types of photoacid generator (PAG) were dissolved in a solvent, and 0.01 to 2.0% by weight of a base additive made of amines (based on the total weight of the polymer) was added thereto to completely dissolve the reactants. Examples of the PAG include inorganic onium salts (0.5 to 3.0% by weight based on the total weight of polymer) and organic sulfonates (1.0 to 10% by weight based on the total weight of polymer), alone or in combination. Examples of the solvent include propylene glycol monomethyl ether acetate (PGMEA) and ethyl lactate (EL), etc., alone or in combination. Thereafter, the solution was filtered using a 0.2 μm membrane filter to obtain a resist composition. Then, the resist composition was coated on a silicon wafer treated with hexamethyldisilazane (HMDS) to a thickness of about 0.3 to 0.5 μm .

- Resist patterning: The coated wafer was pre-baked (soft-baked) at a temperature of 100 to 140°C for 60 to 120 seconds and exposed to light using DUV, e-beam or X-ray, etc. Then, post-exposure baking (PEB) was performed at a temperature of 100 to 150°C for 60 to 120 seconds. Thereafter, the resultant film was developed using 2.38 wt% of tetramethylammonium hydroxide (TMAH) solution for about 10 to 90 seconds to obtain a desired pattern.

- Etching: An underlying layer such as SiO_2 was etched with a predetermined etching gas, for example, halogen gas or C_xF_y gas, using the obtained resist pattern as a mask. Subsequently, the resist pattern remaining on the silicon wafer was stripped to form a desired silicon oxide pattern.

Example 17

Resist composition

5 A resist composition was prepared using 1.0 g of the polymer synthesized in Example 9, 15 mg of triphenylsulfonium triflate (TPSOTf), and 2 mg of triisobutylamine were completely dissolved in 8.0 g of PGMEA and then filtered using a 0.2 μm membrane filter. The obtained resist composition was coated on a Si wafer to a thickness of about 0.3 μm .

Thereafter, the wafer having the resist composition coated thereon was pre-baked at a temperature of 130°C for 90 seconds and exposed to light using an ArF excimer laser (NA= 0.6 and σ = 0.7). Then, post exposure baking (PEB) was performed at a temperature of 130°C for 90 seconds.

10 The resultant film was developed using 2.38 wt% of TMAH solution for 60 seconds to form a resist pattern. When an exposure dose was about 15 mJ/cm², it was observed that a 0.20 μm line and space pattern was obtained.

Example 18

Resist composition

15 A resist composition was prepared using 1.0 g of polymer synthesized in Example 9, 10 mg of TPSOTf, 20 mg of N-succinimidyl triflate and 4 mg of triisobutylamine were completely dissolved in 8.0 g of PGMEA and then filtered using a 0.2 μm membrane filter. The obtained resist composition was coated on a Si wafer to a thickness of about 0.3 μm .

20 Thereafter, a resist pattern was formed in the same manner as in Example 17. When an exposure dose was about 20 mJ/cm², it was observed that a 0.20 μm line and space pattern was obtained.

Example 19

Resist composition

25 A resist composition was prepared using 1.0 g of polymer synthesized in Example 12, 15 mg of TPSOTf, 2 mg of triisobutylamine were completely dissolved in 8.0 g of PGMEA and then filtered using a 0.2 μm membrane filter. The obtained resist composition was coated on a Si wafer to a thickness of about 0.3 μm .

30 Thereafter, the wafer having the resist composition coated thereon was pre-baked at a temperature of 130°C for 90 seconds and exposed to light using an ArF excimer laser (NA= 0.6 and σ = 0.7). Then, PEB was performed at a temperature of 130°C for 90 seconds.

The resultant film was developed using 2.38 wt% of TMAH solution for 60 seconds to form a resist pattern. When an exposure dose was about 18 mJ/cm², it was observed that a 0.20 μm line and space pattern was obtained.

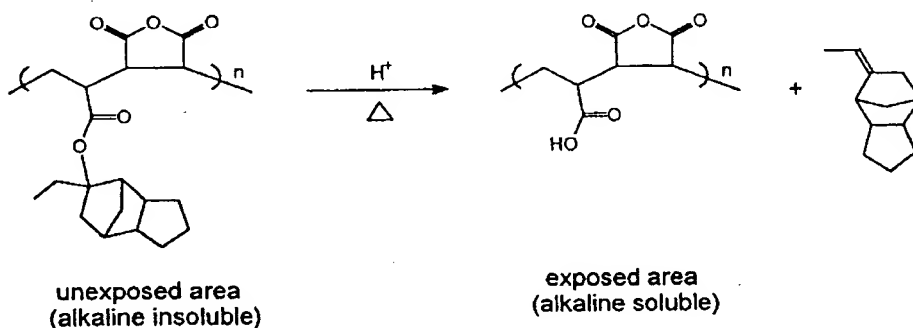
Example 20

Resist composition

Poly(ethylene glycol) (Mw 2,000) was added to the resist compositions obtained in Examples 17, 18, and 19 in an amount of about 200 ppm and then a resist pattern was prepared in the same manner as in Example 17. As a result, when an exposure dose was about 15 to 20 mJ/cm², it was observed that a 0.20 μm line and space pattern was obtained.

Photomechanism of copolymer

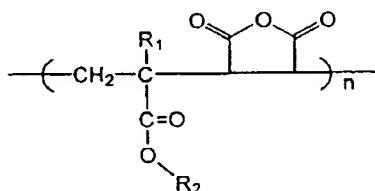
The photomechanism of the resist composition obtained in Example 17 is as follows.



As shown in the above photomechanism, an unexposed portion of the resist composition according to the present invention exhibits a low solubility to a developing solution (low Rmin) due to a dissolution inhibition effect on the developing solution by a bulky alicyclic protecting group, while an exposed portion of the resist composition exhibits a high solubility to the developing solution (high Rmax) due to the decomposition of the bulky alicyclic protecting group in the presence of acid (H⁺). Thus, a resist composition having high contrast can be obtained, thereby achieving a high-resolution, high-sensitivity resist pattern.

What is claimed is:

1. A photosensitive polymer having a mass average molecular weight (Mw) of 3,000-100,000, preferably 5,000-30,000, and represented by the following formula:



wherein

R₁ is hydrogen or methyl group, and

R₂ is an acid-labile group of a tertiary alkyl group, such as tert-butyl group, which can be decomposed by an acid, more preferably a bulky alicyclic acid-labile group.

2. The photosensitive polymer according to claim 1, wherein R₁ is hydrogen or methyl group and R₂ is an aliphatic alicyclic hydrocarbon group of a tertiary alkyl group.

3. The photosensitive polymer according to claim 2, wherein R₁ is hydrogen or methyl group and R₂ is 2-methyl-2-tricyclodecanyl or 2-ethyl-2-tricyclodecanyl group.

4. The photosensitive polymer according to claim 2, wherein R₁ is hydrogen or methyl group and R₂ is 2-methyl-2-adamantyl or 2-ethyl-2-adamantyl group.

5. The photosensitive polymer according to claim 2, wherein R₁ is hydrogen or methyl group and R₂ is 2-methyl-2-isobornyl or 2-ethyl-2-isobornyl group.

6. The photosensitive polymer according to claim 2, wherein R_1 is hydrogen or methyl group and R_2 is 2-methyl-2-norbornyl or 2-ethyl-2-norbornyl group.

5 7. A resist composition comprising the polymer according to claim 1 or 2, a photoacid generator (PAG), and a base additive, wherein the PAG is contained in an amount of 1.0 to 15 % by weight based on the total weight of the polymer and the base additive is contained in an amount of 0.01 to 2.0% by weight based on the total weight of the polymer, and a method of producing a semiconductor device using the resist composition, comprising the following steps:

10 (a) production of a resist film: coating the resist solution on a substrate (Si wafer) and soft-baking (prebaking) the coated substrate to obtain a resist film;

15 (b) resist patterning: exposing the resist film to light using a radiation source, such as DUV, e-beam, x-ray, post-exposure baking (PEB) the substrate, and then, developing the resist film using a developer (tetramethylammonium hydroxide solution) to form a desired resist pattern; and

(c) etching: etching an underlying layer with a dry etching gas (halogen gas or C_xF_y gas, etc.) using the obtained resist pattern as a masking layer and stripping the resist film from the substrate to form a desired pattern.

20 8. The resist composition according to claim 7, wherein the PAG is an inorganic material, such as triarylsulfonium salts and diaryliodonium salts, and an organic material, such as sulfonates, or a mixture thereof.

25 9. The resist composition according to claim 8, wherein the PAG comprises triphenylsulfonium triflate(trifluoromethanesulfonate), diphenyliodonium triflate, triphenylsulfonium nonaflate(nonafluoromethanesulfonate), diphenyliodonium nonaflate, triphenylsulfonium antimonate, diphenyliodonium antimonate, di-t-butyl diphenyliodonium triflate, N-succinimidyl triflate, 30 2,6-dinitrobenzyl sulfonate, or a mixture thereof.

10. The resist composition according to claim 7, wherein the base additive is triethylamine, triisobutylamine, trioctylamine, diethanolamine, triethanolamine or a mixture thereof.

11. The resist composition according to claim 7, further comprising a surfactant, such as polyether or polysulfonate, in an amount of about 50 to 500 ppm.

5 12. The resist composition according to claim 11, wherein further comprising a surfactant, poly(ethylene glycol) in an amount of about 50 to 500 ppm.

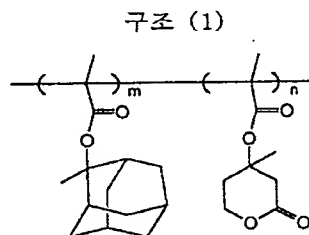
종래 기술의 문제점 및 그것을 해결하고자 하는 본 발명의 목적

(Background Art & Objects of the Invention)

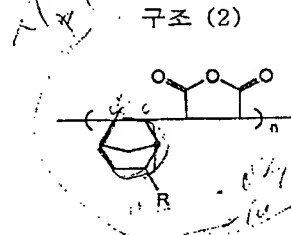
반도체 제조공정의 고집적화에 따른 lithography technology에 있어서 미세패턴 형성의 issue는 필수적인 과제가 되었다. 더욱이 device의 용량이 1G bit DRAM급 이상으로 갈수록 design rule이 $0.2\mu\text{m}$ 이하의 pattern size가 요구됨에 따라 resist material에 있어서도 기존의 KrF excimer laser(248nm)를 이용한 resist material의 한계를 맞게 되었다. 따라서, 새로운 ArF excimer laser(193nm)를 이용한 lithography technology가 등장하였는데, 이러한 ArF lithography에 사용되는 resist material은 기존의 resist material에 비해 상용화하기에는 많은 문제점들을 가지고 있다.

가장 대표적인 문제점으로는 polymer의 투과도(transmittance) 및 dry-etch resistance에 대한 issue를 들 수 있는데, 지금까지 알려진 일반적인 ArF resist로서 (meth)acrylate계 polymer들이 주로 사용되어 왔는데, 이 중에서 초기의 IBM社의 terpolymer system인 poly(methyl methacrylate-tert-butyl methacrylate-methacrylic acid)이 대표적인데, 이러한 polymer들의 심각한 문제점은 dry-etch resistance가 매우 나쁘다는 것이다. 그래서, dry-etch resistance를 증가시키기 위해 여러가지 dry-etching에 강한 물질인 alicyclic compound(isobornyl, adamantyl, tricyclodecanyl group, etc)등을 polymer backbone에 도입하는 방법을 사용하고 있으나, 여전히 etch resistance에 대한 문제를 안고 있었다. 또한, 이러한 alicyclic compound를 사용한 polymer의 특성은 막질에 대한 adhesion특성이 나빠 resist 현상(development)시에 resist pattern의 lifting 현상을 가지고 있었다.

또한, 최근에는 새로운 타입의 polymer로서 Fujitsu사의 alicyclic protecting group를 갖는 methacrylate copolymer구조(구조1)와 IBM사의 cycloolefin-maleic anhydride(COMA) alternating polymer(구조2)가 소개되었는데, 이러한 polymer들에 있어서도 여전히 ArF resist로서의 문제점들을 가지고 있었다. 이것은 그림1과 같은 구조의 polymer들은 dry etching resistance 및 Line Edge Roughness(LER)와 같은 문제점들을 가지고 있으며, 그림2와 같은 polymer들에 있어서는 resist contrast 및 투과도 문제점을 가지고 있었다.



- High contrast
- Line edge roughness
- Poor etch resistance
- High cost



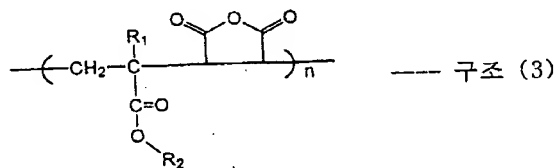
- Good etch resistance
- Low transmittance
- Low synthetic yield
- Poor adhesion

따라서, 본 발명에서는 이러한 기존 polymer들의 문제점들을 극복하고 high lithographic performance를 갖는 resist를 개발하기 위해 새로운 타입의 polymer를 제조하였다. 이것은 polymer의 구조적인 측면에서 bulky alicyclic protecting group를 가진 meth(acrylate) monomer와 maleic anhydride monomer의 공중합체를 제조함으로써, 기존의 cycloolefin-maleic anhydride(COMA) system에 비해 polymer의 투과도(transmittance) 및 합성수율(synthetic yield)면에서 획기적으로 개선된 polymer를 얻을 수 있으며, 더불어 기존의 methacrylate copolymer보다는 etch 내성 및 제조 단가 측면에서 보다 우수한 특성을 보여줄 수 있다.

일반적으로 maleic anhydride monomer의 중합특성은 자체적으로 중합은 진행되지 않기 때문에, 보통 electron-donating group이 치환된 olefin monomer와의 alternating copolymer 형태로 중합이 진행되는 특성을 가지고 있으며, 가장 많이 사용되는 comonomer로서 alkyl vinyl ether와 cycloolefin 등이 알려져 있다. 한편, 본 발명에서는 electron-withdrawing group를 가진 meth(acrylate) monomer와의 공중합체로서, 중합조건 및 monomer 조성비에 따라서 homopolymer 및 copolymer 형태로 polymer를 제조할 수가 있으며, 경우에 따라서는 polymer의 극성을 조절하기 위해 제2, 3의 모노머를 도입하여 terpolymer 이상의 공중합체를 제조할 수도 있다.

특히, 본 발명의 또 다른 특성으로 기존의 cycloolefin-maleic anhydride(COMA) alternating copolymer의 단점인 rigid backbone에 의한 high Tg(유리전이 온도)($>180^{\circ}\text{C}$)로 인한 PED(post-exposure delay) 문제를 개선할 수 있는 polymer backbone를 도입하여 적절한 범위의 Tg($130\sim160^{\circ}\text{C}$)를 가질 수 있기 때문에 공정진행상 annealing effect에 의한 PED 개선효과를 가질 수도 있다. 더불어 cycloolefin monomer 대신에 acrylate monomer를 도입함으로써 보다 적절한 polymer polarity를 보여줌으로써 하부막질에 대한 adhesion 문제도 개선할 수가 있는 장점을 가지고 있다.

본 발명을 좀 더 상세히 기술하면 본 발명에 의한 물질은 아래의 구조식(3)과 같이 이루어지며, 구조식에서 R1은 hydrogen 및 methyl group를 의미하며, R2은 노광에 의해 발생된 산에 의해서 분해가 일어날 수 있는 group을 의미하며, 이중에서도 특히 alicyclic tert-alkyl group를 의미한다. 즉, R2은 2-methyl-2-norbornyl, 2-ethyl-2-norbornyl, 2-methyl-2-isobornyl, 2-ethyl-2-isobornyl, 8-methyl-8-tricyclo[5.2.1.0^{2,6}]decanyl, 8-ethyl-8-tricyclo[5.2.1.0^{2,6}]decanyl, 2-methyl-2-adamantyl, 2-ethyl-2-adamantyl 등과 같이 alicyclic ring 구조를 포함하는 bulky tertiary alkyl group으로, etch resistance의 향상과 dissolution inhibitor 역할을 한다. 그리고 maleic anhydride 모노머를 도입하여 adhesion promoter 및 wettability 향상 등의 역할을 한다.



결론적으로, 본 발명에 따른 copolymer를 제조함으로써, 기존 polymer들이 가지고 있는 문제점들을 해결할 수 있는 polymer를 제조할 수 있었으며, polymer 제조면에서도 보다 간편하고 값싸게 만들수가 있기 때문에 향후 이러한 polymer를 이용한 resist composition을 이용해 여러 가지 형태의 photolithographic process에 적용할 경우 매우 우수한 lithographic performance를 보여줌으로써, 향후 차세대 반도체 device를 만드는 데 매우 유용하게 사용될 수 있다.

발명의 구체적 설명

- 발명의 목적을 달성하기 위해 어떻게 구현했는가?
(實 TEST 혹은 Simulation에 의해 검증된 구체적 회로 구조 또는 제조방법 및 조건에 대하여 그 작용 또는 제조수순을 따라 상세히 명기할 것)
- 각 작용과 함께 발생하는 특유의 효과를 병행 기록할 것

(Detailed Disclosure of the Invention)

실시예1) Synthesis of 8-ethyl-8-tricyclodecanol

- 500mL three neck round-bottom flask에 ethylmagnesium bromide(1.0M solution in diethyl ether) 200mL를 넣고 여기에 tricyclodecan-8-one(30g, 0.2mol)를 diethyl ether에 녹여서 dropping funnel를 이용하여 상온에서 천천히 떨어뜨린 다음, reflux condition에서 12시간 정도 반응시킨다.
- 반응이 끝난 후, 반응물을 과량의 물에 pouring시킨다음, HCl를 이용해 중화시키고 diethyl ether를 이용해 extraction한 다음, magnesium sulfate를 이용해 drying한 후에 solvent를 날리고 이어서 crude product를 column chromatography(ethyl acetate:n-hexane=1:3)를 이용해 product를 얻는다.
(yield; 65%)

실시예2) Synthesis of 8-ethyl-8-tricyclodecanyl acrylate

- 실시예1)에서 합성한 8-ethyl-8-tricyclodecanol(18g, 0.1mol)과 triethylamine(11g, 0.11mol)를 anhydrous THF(200mL)에 녹인다음, 여기에 acryloyl chloride(10g, 0.11mol)를 상온에서 천천히 첨가한 다음, 약 12시간 정도 반응시킨다.
- 반응이 끝난 후, 과량의 solvent를 날리고 반응물을 과량의 물에 pouring시킨 다음, HCl를 이용하여 중화시킨 후 diethyl ether를 이용해 추출한 다음, MgSO₄를 이용해 drying한다. 그런다음, solvent를 날리고 crude product를 vacuum distillation를 이용해 product를 분리한다.
(yield; 75%)

실시예3) Synthesis of 8-ethyl-8-tricyclodecanyl methacrylate

- 실시예1)에서 합성한 8-ethyl-8-tricyclodecanol(18g, 0.1mol)과 triethylamine(11g, 0.11mol)를 anhydrous THF(200mL)에 녹인다음, 여기에 methacryloyl chloride(0.11mol)를 실시예2)와 같은 방법으로 반응시켜 product를 분리한다. (yield; 75%)

실시예4) Synthesis of 8-methyl-8-tricyclodecanyl acrylate

- 실시예1)의 방법으로 methylmagnesium bromide solution를 이용해 8-ethyl-8-tricyclodecanol를 합성한 다음, 이를 이용해 실시예2)와 같은 방법을 사용하여 product를 합성한다.

실시예5) Synthesis of 2-methyl-2-adamantyl acrylate

- 2-methyl-2-adamantanol(17g, 0.1mol)과 triethylamine(11g, 0.11mol)를 anhydrous THF(250mL)에 녹인다음, 여기에 acryloyl chloride(10g, 0.11mol)를 상온에서 천천히 첨가한 다음, 약 12시간 정도 반응시킨다.

- 반응이 끝난 후, 과량의 solvent를 날리고 반응물을 과량의 물에 pouring시킨 다음, HCl를 이용하여 중화시킨 후 diethyl ether를 이용해 추출한 다음, MgSO₄를 이용해 drying한다. 그런다음, solvent를 날리고 crude product를 vacuum distillation를 이용해 product를 분리한다.

(yield; 75%)

실시예6) Synthesis of 2-methyl-2-adamantyl methacrylate

- 2-methyl-2-adamantanol(17g, 0.1mol)과 triethylamine(11g, 0.11mol), 그리고 methacryloyl chloride(0.11mol)를 anhydrous THF(250mL)에서 실시예5)와 같은 방법으로 product를 얻는다.

(yield; 75%)

실시예7) Synthesis of 2-methyl-2-isobornyl acrylate

- methyllithium(1.0M solution in diethyl ether) solution(200mL)에 camphor(0.2mol in diethyl ether) solution를 dropping funnel를 이용하여 상온에서 천천히 떨어뜨린 다음 약 2시간 정도 반응시킨 다음, 여기에 acryloyl chloride(20g, 0.22mol)를 상온에서 천천히 첨가한 다음, reflux condition에서 약 12시간 정도 반응시킨다.

- 반응이 끝난 후, 반응물을 과량의 물에 pouring시킨다음, HCl를 이용해 중화시키고 diethyl ether를 이용해 extraction한 다음, magnesium sulfate를 이용해 drying한 후에 solvent를 날리고 이어서 crude product를 vacuum distillation를 이용해 product를 분리한다.

(yield; 65%)

실시예8) Synthesis of 2-methyl-2-norbornyl acrylate

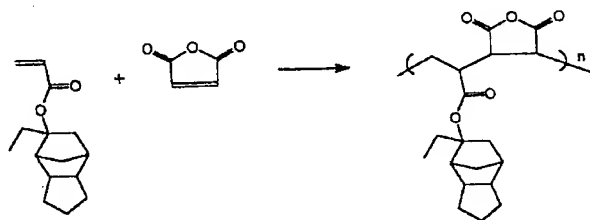
- methyllithium(1.0M solution in diethyl ether) solution(200mL)과 norcamphor(0.2mol in diethyl ether) solution, 그리고 acryloyl chloride(20g, 0.22mol)를 실시예7)과 같은 방법으로 반응시킨 다음, product를 분리한다. (yield; 65%)

발명의 구체적 설명

- 발명의 목적을 달성하기 위해 어떻게 구현했는가?
(實 TEST 혹은 Simulation에 의해 검증된 구체적 회로 구조 또는 제조방법 및 조건에 대하여 그 작용 또는 제조수순을 따라 상세히 명기할 것)
- 각 작용과 함께 발생하는 특유의 효과를 병행 기록할 것

(Detailed Disclosure of the Invention)

실시예9) Copolymer synthesis



- 실시예2)에서 합성한 8-ethyl-8-tricyclodecanyl acrylate(7.03g, 30mmol)와 maleic anhydride(2.94g, 30mmol)를 AIBN(azobisisobutyronitrile)(1mol%)과 함께 anhydrous THF(40g)에 녹인 다음, nitrogen gas를 이용해 1시간 정도 purge시킨 다음, 70°C 온도에서 약 12시간 정도 중합시킨다.

- 중합이 끝난 후, 반응물을 과량의 n-hexane에 천천히 떨어뜨리면서 침전시킨 다음, 침전물을 다시 THF에 녹인 후, cosolvent(n-hexane:isopropyl alcohol=1:1) system에서 2회 침전을 시킨 뒤, 침전물을 50°C의 vacuum oven에서 약 24시간 동안 말린다. (yield; 70%)

중량 평균분자량(Mw)= 11800, polydispersity= 2.1

실시예10) Copolymer synthesis

- 실시예3)에서 합성한 8-ethyl-8-tricyclodecanyl methacrylate(30mmol)와 maleic anhydride(30mmol)를 AIBN(1mol%)과 함께 실시예9)와 같은 방법으로 중합시킨 다음, polymer를 얻는다.
(yield; 65%)

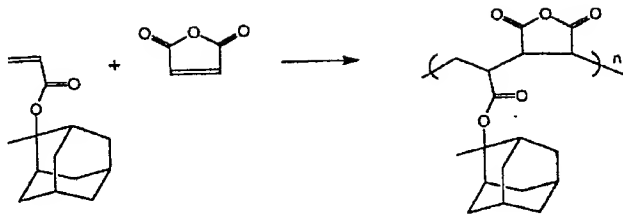
중량 평균분자량(Mw)= 12300, polydispersity= 2.1

실시예11) Copolymer synthesis

- 실시예4)에서 합성한 8-methyl-8-tricyclodecanyl acrylate(30mmol)와 maleic anhydride(30mmol)를 AIBN(1mol%)과 함께 실시예9)와 같은 방법으로 중합시킨 다음, polymer를 얻는다.
(yield; 70%)

중량 평균분자량(Mw)= 12300, polydispersity= 2.1

실시예12) Copolymer synthesis



- 실시예5)에서 합성한 2-methyl-2-adamantyl acrylate(6.61g, 30mmol)와 maleic anhydride(2.94g, 30mmol)를 AIBN(1mol%)과 함께 anhydrous THF(40g)에 녹인다음, nitrogen gas를 이용해 1시간 정도 purge시킨 다음, 70°C 온도에서 약 12시간 정도 중합시킨다.

- 중합이 끝난 후, 반응물을 과량의 n-hexane에 천천히 떨어뜨리면서 침전시킨 다음, 침전물을 다시 THF에 녹인 후, cosolvent(n-hexane:isopropyl alcohol=1:1) system에서 2회 침전을 시킨 뒤, 침전물을 50°C의 vacuum oven에서 약 24시간 동안 말린다.

(yield; 70%)

※ 중량 평균분자량(Mw)= 11100, polydispersity= 2.0

실시예13) Copolymer synthesis

- 실시예7)에서 합성한 2-methyl-2-isobornyl acrylate(30mmol)와 maleic anhydride(30mmol)를 AIBN(1mol%)과 함께 실시예12)와 같은 방법으로 중합시킨 다음, polymer를 얻는다.

(yield; 70%)

※ 중량 평균분자량(Mw)= 10800, polydispersity= 2.2

실시예14) Copolymer synthesis

- 실시예8)에서 합성한 2-methyl-2-norbornyl acrylate(30mmol)와 maleic anhydride(30mmol)를 AIBN(1mol%)과 함께 실시예12)와 같은 방법으로 중합시킨 다음, polymer를 얻는다.

(yield; 70%)

※ 중량 평균분자량(Mw)= 12100, polydispersity= 2.1

실시예15) Terpolymer synthesis

- 실시예3)에서 합성한 8-ethyl-8-tricyclodecanyl methacrylate(35mmol)와 maleic anhydride(40mmol), 그리고 methacrylic acid(5mmol)를 AIBN(1mol%)과 함께 실시예12)와 같은 방법으로 중합시킨 다음, polymer를 얻는다.

(yield; 70%)

※ 중량 평균분자량(Mw)= 12400, polydispersity= 2.1

特許 圖面 用紙

주의사항

1. 발명의 특징을 가장 잘 나타낼 수 있는 것을 제1도로하며, 발명의 중요한 부분의 명칭과 도면상의 부호를 통일시켜 기입한다.
2. 종래 기술에 대한 도면도 기입한다.
3. 도면의 용지가 필요이상 증가되지 않도록 Layout을 조정한다.

직무발명신고서양식 #5 (Drawings)

실시예16) Resist composition for patterning process

- Resist coating: 실시예9~15)에서 합성한 polymer(12~15wt% solid content to solvent)들을 여러 가지 inorganic onium salts(0.5~3.0wt% to polymer) 혹은 organic sulfonates(1.0~10wt% to polymer) 타입의 PAG(photoacid generator)를 단독 혹은 혼합형태로 propylene glycol monomethyl ether acetate(PGMEA) 또는 ethyl lactate(EL) 등의 단독 혹은 혼합 solvent에서 녹인다음, 여러 가지 base additive(amine류)(0.01~2.0wt% to polymer)를 첨가하여 완전히 녹인다. 그런다음, 0.2 μ m membrane filter를 이용해 resist solution를 거른다음, HMDS(hexamethyldisilazane)를 처리한 Si wafer에 약 0.3~0.5 μ m 두께로 coating한다.

- Resist patterning: 100~140°C의 온도범위에서 60~120sec 동안 pre-baking(soft baking)를 실시한 후, DUV, e-beam, x-ray 등을 이용하여 resist film를 노광한 다음, 100~150°C의 온도범위에서 60~120sec동안 post-exposure bake(PEB)를 실시한다.

그런다음, 2.38wt% TMAH(tetramethylammonium hydroxide) solution를 이용해 약 10~90sec동안 현상하여 원하는 pattern를 형성한다.

- Etching: 생성된 resist pattern를 masking layer로 하여 특성 etch gas(halogen, CxFy 등)를 사용하여 하부막질(예, SiO₂)를 etching한 후, 남아있는 resist film를 strip하여 필요로 하는 pattern를 형성한다.

실시예17) Resist Composition

- 실시예9)에서 합성한 polymer(1.0g)와 triphenylsulfonium triflate(TPSOTf)(15mg), 그리고 triisobutylamine(2mg)를 PGMEA(8.0g) solvent에 넣어 완전히 녹인다음, 0.2 μ m membrane filter를 이용해 resist solution를 거른다음, Si wafer에 약 0.3 μ m 두께로 coating한다.

- 130°C 온도에서 90sec 동안 soft baking를 실시한 후, ArF excimer laser(NA 0.6, σ 0.7)를 이용해 노광한 다음, 130°C 온도에서 90sec 동안 PEB를 실시한다.

- 그런다음, 2.38wt% TMAH solution으로 60sec동안 현상한 결과, 약 15mJ/cm²의 dose에서 0.20 μ m lines and spaces pattern를 확인하였다.

실시예18) Resist Composition

- 실시예9)에서 합성한 polymer(1.0g)와 triphenylsulfonium triflate(TPSOTf)(10mg), 그리고 N-succinimidyl triflate(20mg)를 triisobutylamine(4mg)과 함께 PGMEA(8.0g)에 넣어 완전히 녹인다음, 0.2 μ m membrane filter를 이용해 resist solution를 거른다음, Si wafer에 약 0.3 μ m 두께로 coating한다.

- 실시예17)과 같은 조건에서 노광한 결과, 약 20mJ/cm²의 dose에서 0.20 μ m lines and spaces pattern를 확인하였다.

실시예19) Resist Composition

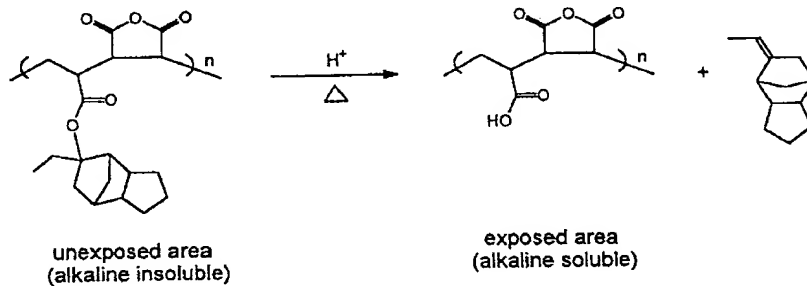
- 실시예12)에서 합성한 polymer(1.0g)와 triphenylsulfonium triflate(TPSOTf)(15mg), 그리고 triisobutylamine(2mg)를 PGMEA(8.0g) solvent에 넣어 완전히 녹인다음, 0.2 μ m membrane filter를 이용해 resist solution를 거른다음, Si wafer에 약 0.3 μ m 두께로 coating한다.
- 130°C 온도에서 90sec 동안 soft baking를 실시한 후, ArF excimer laser(NA 0.6, σ 0.7)를 이용해 노광한 다음, 130°C 온도에서 90sec 동안 PEB를 실시한다.
- 그런다음, 2.38wt% TMAH solution으로 60sec동안 현상한 결과, 약 18mJ/cm²의 dose에서 0.20 μ m lines and spaces pattern를 확인하였다.

실시예20) Resist Composition

- 실시예17, 18, 19)의 resist 조성물에 poly(ethyleneglycol)(Mw=2,000)를 약 200ppm정도 첨가한 다음, 실시예17)과 같은 조건으로 공정을 진행한 결과, 약 15~20mJ/cm²의 dose에서 0.20 μ m lines and spaces pattern를 확인하였다.

Photomechanism of copolymer

- 실시예17)의 resist 조성물의 노광 mechanism를 하기식에서 나타내었다.



그림에서 보듯이 비노광부에서는 bulky alicyclic protecting group에 의해 현상액에 대한 dissolution inhibition effect가 작용하여 낮은 용해도(low Rmin)를 가지며, 반대로 노광부에서는 bulky alicyclic protecting group이 acid(H⁺) 존재하에서 분해가 일어나 현상액에 대한 높은 용해도 (high Rmax)를 나타내 high contrast를 가지는 resist를 얻을 수 있으며, 이로 인해 높은 해상도 및 고감도용 resist pattern를 얻을 수가 있다.

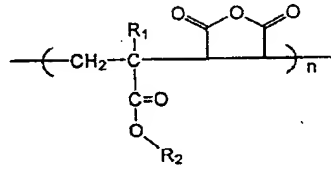
特許 圖面 用紙

주의사항

1. 발명의 특징을 가장 잘 나타낼 수 있는 것을 제1도로하며, 발명의 중요한 부분의 명칭과 도면中的 부호를 통일시켜 기입한다.
2. 종래 기술에 대한 도면도 기입한다.
3. 도면의 용지가 필요이상 증가되지 않도록 Layout을 조정한다.

직무발명신고서양식 #5 (Drawings)

1. 하기식과 같은 구조의 photosensitive polymer:



여기서, R₁는 hydrogen, methyl group이며,

R₂는 tert-butyl group과 같은 acid 존재하에서 분해가 일어날 수 있는 tertiary alkyl의 acid-labile group이며, 보다 적절하게는 bulky alicyclic acid-labile group임.

그리고 질량 평균분자량(Mw)이 3,000 ~ 100,000사이의 범위를 가지며, 보다 적절한 범위는 5000~30000사이의 값을 가짐.

2. 제1항에 있어 R₁는 hydrogen, methyl group이며, R₂가 tertiary alkyl group의 aliphatic alicyclic hydrocarbon인 photosensitive polymer.
3. 제2항에 있어 R₁는 hydrogen, methyl group이며, R₂가 2-methyl-2-tricyclodecanyl, 2-ethyl-2-tricyclodecanyl group인 photosensitive polymer.
4. 제2항에 있어 R₁는 hydrogen, methyl group이며, R₂가 2-methyl-2-adamantyl, 2-ethyl-2-adamantyl group인 photosensitive polymer.
5. 제2항에 있어 R₁는 hydrogen, methyl group이며, R₂가 2-methyl-2-isobornyl, 2-ethyl-2-isobornyl group인 photosensitive polymer.
6. 제2항에 있어 R₁는 hydrogen, methyl group이며, R₂가 2-methyl-2-norbornyl, 2-ethyl-2-norbornyl group인 photosensitive polymer.

7. 제1항 및 2항의 polymer들과 photoacid generator(PAG), 그리고 base additive를 사용한 레지스트 조성물 및 이를 이용한 반도체 제조공정:

여기서, 사용된 PAG의 양은 사용한 polymer 무게비의 1.0~15wt% 사이의 양을 사용하며, 그리고 base additive의 양은 사용한 polymer 무게비의 0.01 ~ 2.0wt% 사이의 양을 사용하며, 그리고 patterning 공정은 다음과 같은 단계를 말함.

a) Resist film 제조단계: resist solution를 substrate(Si wafer) 표면에 도포한 다음, soft baking(prebaking)를 통하여 resist film를 만드는 단계.

b) Resist patterning 단계: 형성된 resist film를 여러 가지 radiation source(DUV, e-beam, x-ray 등)를 이용하여 노광한 후에 post-exposure bake(PEB)를 거친 다음, developer(tetramethylammonium hydroxide solution)로 현상하여 원하는 resist pattern를 형성하는 단계.

c) Etching 단계: 형성된 resist pattern를 masking layer로 하여 dry etching gas(halogen, CxFy 등)를 사용하여 하부 막질을 etching한 다음, resist film를 strip하여 원하는 pattern를 만드는 단계.

8. 제7항에서 언급한 photoacid generator는 triarylsulfonium salts, diaryliodonium salts와 같은 inorganic type과 sulfonates와 같은 organic type를 단독 혹은 혼합으로 사용한 레지스트 조성물.

9. 제8항에서 언급한 PAG로 triphenylsulfonium triflate(trifluoromethanesulfonate), diphenyliodonium triflate, triphenylsulfonium nonaflate(nonafluoromethanesulfonate), diphenyliodonium nonaflate, triphenylsulfonium antimonate, diphenyliodonium antimonate, di-t-butylidiphenyliodonium triflate, 그리고 N-succinimidyl triflate, 2,6-dinitrobenzyl sulfonates 등과 같은 compound를 단독 혹은 혼합으로 사용한 resist 조성물.

10. 제7항에서 사용한 base additive로 triethylamine, triisobutylamine, trioctylamine, diethanolamine, triethanolamine 등을 단독 혹은 혼합으로 사용한 resist 조성물.

11. 제7항의 resist 조성물에 polyether 및 polysulfonates와 같은 surfactants를 50~500ppm 정도 첨가한 레지스트 조성물.

12. 제11항에 있어서 poly(ethylene glycol)를 surfactants를 50~500ppm정도 첨가한 레지스트 조성물.